

## 8. INTERSTITIAL WATER STUDIES, LEG 15 – MAJOR IONS Br, Mn, NH<sub>3</sub>, Li, B, Si, AND $\delta C^{13}$

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### INTRODUCTION AND PROCEDURES

Details of the shipboard geochemical work as well as comparisons and interpretations of data collected on board ship and on shore can be found elsewhere in this volume. This report concerns only data obtained at UCLA and TAMU, and gives only a minimum of interpretation.

A total of seventy samples of pore water were received at UCLA. These consisted of from 5 to 9 ml of filtered water sealed in plastic syringes, which had been kept refrigerated except for time in shipment. Work began on the samples soon after their arrival, but this was as long as three months after collection. The large number of samples, and technical problems, made it necessary to refrigerate some of the samples for an additional three to five months before they could be analyzed.

The samples were opened at UCLA and an aliquot of water was removed for total CO<sub>2</sub>,  $\delta C^{13}$ , and sulfate determinations, following procedures given in Presley and Claypool (1971). The remaining water from each sample was sent to TAMU where it was analyzed for Cl, Br, B, NH<sub>3</sub>, Si, Na, Mg, Ca, K, Li, and Mn following procedures given by Presley (1971). This was the first group of samples analyzed at TAMU, and some of the scatter in the data can be attributed to problems arising from new equipment, new technicians and the like. An additional factor to consider is that the samples were not all analyzed at once, but rather in several batches over several months time.

### RESULTS AND DISCUSSION

All the data we have obtained to date is given in Tables 1 and 2. Major cation concentrations are given for comparison with the values obtained by other groups. Few duplicate analyses were done because of the small sample size and the large number of samples. Thus, it is difficult to evaluate the significance of isolated high or low values. There is little doubt, however, that trends of increasing or decreasing concentration with increasing depth in the sediment column, a common phenomenon at many of the Leg 15 sites, are valid.

#### Chloride and Bromide

Most of the Leg 15 samples were found to have chloride and bromide concentrations within 5 per cent of those shown by average surface seawater. However, samples at depth at two sites proved to be highly abnormal. At Site 147, drilled in the Cariaco Trench near the coast of Venezuela, the pore water seems to be slightly depleted in Br relative to Cl down to a depth of 14 meters. Below that depth Br concentration increases sharply, rising to a maximum of 178 ppm at 148 meters, our deepest sample.

This increase in Br is accompanied by a decrease in Cl, resulting in a Cl/Br ratio only about one-third that of seawater at the bottom of the hole. A similar, but less drastic, situation was found at Site 154, drilled in the Colombian Basin just north of Panama. Thus, the two unusual sites were the two sites drilled nearest to shore. Fresh water influx from shore may be partly responsible for these unusual pore waters, especially in the case of the Colombian Basin site, because the chlorinity dropped to 14.86 per mil at the bottom of the hole.

#### Sulfate

Every site showed sulfate loss at depth, however the greatest change was again found at the two nearshore sites. The Cariaco Trench is an anoxic basin; therefore, sulfate loss would be expected, and was noted, in the shallowest sediments recovered. It is somewhat surprising that sulfate never completely disappears at this site, although it is lowered to only a few percent of the seawater value. This small amount of sulfate could represent oxidation of sulfide during squeezing, but the sample at 14 meters depth contained too much sulfate to explain in this way. This sample may have been deposited under reducing conditions, judging by the absence of benthic foraminifera. Either the 28,000 years since deposition has not been long enough for the sulfate to be totally reduced by the small amount of organic matter in the sample, or has not had enough time to completely diffuse away. It is not clear whether this slow loss of sulfate at great depth in the sediment column is organically or inorganically controlled. We hope to learn more about this process by studying the sulfur isotope ratios in these samples.

#### Sodium, Magnesium, Calcium, and Potassium

Mg, Ca, and K concentrations in the interstitial waters show large variations from seawater values in these samples, a phenomenon which has been common at many sites on previous legs. Also as usual, there is no significant variation in the Na to Cl ratio within the precision of detection. At Site 154, where the Cl concentration decreases by approximately 25 percent going down the hole, a corresponding drop in Na was found. Na thus appears to be relatively inert to the changes that affect the other three major cations.

Sites 147, 148, and 154 exemplify the phenomenon, previously discussed in some detail by Presley and Kaplan (1968), of Ca loss from pore water in reducing sediments, presumably by CaCO<sub>3</sub> precipitation caused by the increase in total dissolved carbonate species and alkalinity which accompanies sulfate reduction. The shallowest sample that we obtained at Site 147, reportedly from a depth of only 1

TABLE 1  
Trace Element and Isotope Data

Sample	Depth <sup>a</sup> (m)	Mn (mg/kg)	NH <sub>3</sub> (μg/kg)	Li (mg/kg)	B (mg/kg)	Si (mg/kg)	ΣCO <sub>2</sub> (mM/kg)	δC <sup>13</sup> (PDB)
147B-1-2	2.5	0.1	6.2	190	3.5	17.2	12.63	-15.99
147B-1-3	4.25	0.1	31.8	165	6.0	20.3	14.79	-17.63
147B-1-4	4.75	0.1	30.1		3.7	8.0	7.13	-18.43
147-2-3,4	8.5	0.1	16.6	162	3.9	14.0	15.59	-16.44
147B-2-2	15	0.1		165	3.8	11.0	6.44	-13.98
147B-2-6	21	0.1		165	3.1	13.0	12.32	-9.34
147-4-3,4	28	<0.1	13.1	232	3.1	17.0	11.93	-3.55
147B-7-4	63	<0.1	87.3	572	1.5	5.3	16.72	+8.41
147B-9-4	84	<0.1	83.7	600	1.9	6.1	17.04	+5.44
147B-11-3	100	<0.1		590	0.6	6.0	14.29	+8.09
147C-2-1	126	<0.1	87.3	731	1.2	7.6	19.04	+6.54
147C-4-4	148	<0.1	109.8	904	1.5	17.9	18.60	+6.44
148-1-4	6	1.1	1.5	205	5.4	10.2	2.56	-13.07
148-1-4	6	1.2	1.3	197	4.3	8.0	-	-12.16
148-2-1	10	0.36	4.8	205	4.8	6.8	3.05	-14.11
148-2-3	13	0.43	6.6	169	3.6	5.8	4.12	-14.57
148-3-3	22	<0.1	5.7	192	4.1	7.4	4.94	-13.34
148-4-3	31	0.40	6.5	182	3.5	7.2	4.48	-13.44
148-5-2	39	0.1	12.0	170	3.5	6.6	6.03	-
148-6-4	51	0.22	8.2	190	3.2	6.0	5.73	-15.76
148-7-3	59	0.24	17.2	160	3.2	6.7	6.54	-14.95
148-8-3	67	0.22	10.2	165	2.8	5.9	7.35	-17.46
148-9-4	79	<0.1	22.0	170	2.2	3.4	4.03	-17.13
148-10-3	86	0.2	20.3	145	2.1	4.6	6.45	-19.85
148-14-3	122	<0.1	26.5	115	2.1	6.7	4.82	-18.93
148-16-3	141	0.1	30.0	135	1.8	5.5	3.36	-
148-26-2	232	<0.1	17.5	170	2.5	2.7	2.59	-14.35
149-2-2	4	-		250	4.9	-	1.63	-12.78
149-2-5	8	2.9	1.33	170	4.6	3.0	1.63	-13.19
149-3-5	17	4.1	2.98	135	4.8	3.4	2.47	-4.04
149-3-5	17	4.2	0.44	179	5.4	4.7	-	-
149-5-3	32	2.9	2.66	120	4.1	2.6	2.07	-8.75
149-6-4	43	1.8	4.27	125	4.0	2.5	1.87	-8.26
149-7-2	49	2.0	4.19	130	4.0	2.8	1.31	-10.25
149-8-4	62	-	2.2	145	4.7	-	1.42	-10.63
149-9-5	72	2.3	5.00	145	3.5	3.4	1.00	-13.56
149-10-2	78	5.0	4.11	145	3.1	3.1	0.92	-17.54
149-11-4	90	5.0	2.66	165	3.8	2.8	1.07	-14.98
149-12-5	100	-	3.4	185	-	-	1.19	-
149-14-3	116	4.9	1.90	220	3.3	3.4	0.86	-18.21
149-16-4	135	4.8	8.83	330	4.0	5.6	2.09	-
149-18-3	153	4.5	4.55	330	4.0	8.5	1.66	-9.87
149-20-4	173	4.1	6.41	440	4.3	10.1	2.31	-6.64
149-23-4	201	0.9	8.18	465	3.9	17.0	2.93	-11.48
149-26-2	226	0.6	7.62	450	3.9	23.0	2.73	-1.58
149-29-3	254	0.7	10.8	380	3.9	23.6	2.75	-1.22
149-31-1	271	0.9	4.88	330	4.3	26.0	2.75	-6.66
149-31-1	271	-	4.27	-	4.7	28.0	2.92	-0.66
149-35-4	313	0.9	6.61	250	4.6	25.0	2.65	-3.69
149-37-3	329	0.9	0.2(?)	250	4.7	26.0	2.12	-15.02
149-40-1	354	0.8	2.82	240	4.7	26.0	19.03	-
149-41-5	369	0.8	3.15	240	5.0	28.0	2.16	-8.59
149-42-2	374	-				26.1	1.92	-5.83
150-1-4	55	0.4	1.65	185	5.3	4.3	4.35	-16.15
150-2-3	81	1.6	0.35	190	5.6	4.8	2.85	-8.54
150-3-3	89	2.2	0.15	200	-	5.9	2.76	-8.35
150-5-6	113	0.8	0.16	210	-	12.7	2.37	-7.87
151-1-5	68	0.2	0.40	220	5.6	3.6	1.09	+2.98
151-2-2	120	0.1	0.54	325	-	4.7	2.47	-6.79
152-2-4	167	0.15	0.10	170	4.7	18.5	2.15	-1.05
154A-4-4	35	0.11	0.52	110	4.9	5.3	5.59	-21.09
154A-8-0	68	0.22	0.90	195	4.4	8.9	3.54	-11.70
154-2-5	115	0.12	3.40	250	3.9	4.3	1.17	-5.88
154A-16-5	150	0.35	2.25	240	-	6.5	0.14	-
154-5-5	188	0.50	1.95	235	-	9.0	1.24	-2.02
154-14-1	269	0.40	2.50	330	2.9	9.1	1.44	-

<sup>a</sup>Depth in sediment column.

TABLE 2  
Major Element Data

Sample	Depth <sup>a</sup> (m)	Cl (g/kg)	Br (mg/kg)	SO <sub>4</sub> (g/kg)	Na (g/kg)	Mg (g/kg)	Ca (g/kg)	K (g/kg)
147B-1-2	2.5	20.88	61	1.30	11.25	1.268	0.274	0.341
147B-1-3	4.25	20.16	68	0.46	—	1.246	0.166	—
147B-1-4	4.75	20.03	66	0.27	10.90	1.216	0.123	0.324
147B-1-4	5			0.16				
147-2-3,4	8.5		63	0.50	10.67	1.165	0.141	0.303
147B-2-2	15	20.21	58	2.39	11.02	1.343	0.373	—
147B-2-6	21	20.03	70	0.06	10.87	1.074	0.102	—
147-4-3,4	28		75	0.08	10.72	1.022	0.243	0.309
147B-7-4	63	19.32	122	0.11	10.57	0.749	0.124	0.355
147B-9-4	84	18.86	132	0.09	10.44	0.673	0.065	0.341
147B-11-3	100	18.55	120	0.13				
147C-2-1	126	19.00	165	0.31	10.87	0.738	0.033	0.352
147C-4-4	148	18.29	178	0.30	10.35	0.660	0.030	0.344
148-1-4	6	20.24	67	2.38	10.79	1.335	0.409	0.383
148-1-4	6		68					
148-2-1	10	19.47	67	2.40	10.66	1.323	0.342	
148-2-3	13	19.60	66	2.33	10.47	1.281	0.316	0.351
148-3-3	22	19.66	67	2.08		1.241	0.379	
148-4-3	31	19.96	66	2.02	10.66	1.299	0.329	0.331
148-5-2	39	19.73	69	1.55		1.251	0.291	
148-6-4	51	20.24	65	1.65	10.71	1.256	0.281	0.295
148-7-3	59	19.70	69	1.05		1.280	0.264	
148-8-3	67	19.89	70	—	10.61	1.188	0.249	0.262
148-9-4	79	19.45	67	0.81		1.101	0.173	
148-10-3	86	19.96	64	0.89	10.41	1.121	0.250	0.255
148-14-3	122	19.51	69	0.51		1.009	0.264	0.238
148-16-3	141	20.10	67	0.37	10.50	0.928	0.335	0.212
148-26-2	232	19.48	73	0.35		0.951	0.416	
149-2-2	4		65	2.61	10.76	1.333	0.413	
149-2-5	8	19.40	63	2.79	10.87	1.302	0.429	0.385
149-3-5	17	19.89	66	2.65	10.88	1.251	0.479	0.383
149-3-5	17	19.57	65	—	10.80	1.179	0.479	0.380
149-4-3	22		67	2.73	10.86	1.299	0.467	
149-5-3	32	19.57	66	2.67	10.87	1.266	0.513	0.353
149-6-4	43	19.75	66	2.57	10.81	1.225	0.533	0.331
149-7-2	49	19.53	64	2.68	10.87	1.214	0.528	0.331
149-8-4	62	19.67	68	2.17	10.86	1.202	0.553	0.310
149-9-5	72	19.71	66	2.59	10.77	1.211		0.298
149-10-2	78	19.57	64	2.57	10.81	1.191		0.285
149-11-4	90	19.64	64	2.61	10.76	1.184	0.667	0.276
149-12-5	100	17.20	62	1.99	—			0.228
149-14-3	116	19.53	64	2.45	10.66	1.072	0.859	0.217
149-16-4	135	19.57	64	2.34	10.76	1.029	0.839	0.204
149-18-3	153	19.78	66	2.50	10.81	1.022	0.887	0.279
149-20-4	173	19.96	67	2.24	10.95	0.883	1.103	0.244
149-23-4	201	19.85	66	2.26	11.02	0.871	1.183	0.235
149-26-2	226	19.90	67	2.11	10.95	0.841	1.214	0.232
149-29-3	254	19.90	67	2.01	10.87	0.806	1.046	0.218
149-31-1	271	20.10	68	2.15	10.96	0.815	1.224	0.225
149-31-1	271	20.03	68	2.28	11.02	0.826	1.282	0.262
149-35-4	313	20.14	69	2.21	11.03	0.840	1.234	0.213
149-37-3	329	20.07	69	2.12	11.24	0.816	1.239	0.209
149-40-1	354	19.50	67	2.14	10.77	0.809	1.284	0.190
149-41-5	369	20.14	69	1.85	10.97	0.803	1.263	0.192
149-42-2	374	19.87	70	1.69	11.10	0.816	1.145	0.178
150-1-4	55	19.82	65	2.47	11.51	1.249	0.463	0.425
150-2-3	81	19.58	67	2.27	11.51	1.242	0.510	0.375
150-3-3	89	19.65	65	2.17	11.24	1.258	0.510	0.335
150-5-6	113	19.65	66	2.42	11.00	1.201	0.510	0.425
151-1-5	69	20.10	65	2.56	11.35	1.178	0.410	0.480
151-2-2	120	19.65	65	1.83	10.76	1.093	0.470	0.410

TABLE 2 — Continued

Sample	Depth (m)	Cl (g/kg)	Br (mg/kg)	SO <sub>4</sub> (g/kg)	Na (g/kg)	Mg (g/kg)	Ca (g/kg)	K (g/kg)
152-2-4	167	19.82	67	2.65	10.76	1.171	0.586	0.425
154A-4-4	35	18.62	72	0.10	10.52	0.942	0.153	0.380
154A-8-0	68	17.93	79	0.11	10.01	0.899		0.355
154-2-5	115	17.75	79	0.40	9.68	0.848		0.290
154A-16-5	150	16.55	84	0.13	8.98	0.725	0.698	0.190
154-5-5	188	15.34	77	0.16	8.39	0.628		0.160
154-14-1	269	14.86	70	0.27	8.44	0.543		0.165

<sup>a</sup>Depth in sediment column.

meter, has lost one-third its Ca, relative to seawater and the concentration further decreases with depth, leaving the deepest sample depleted by 90 percent.

At Site 154, our shallowest sample, from 35 meters depth, was depleted in Ca by 60 percent, relative to seawater. Unfortunately, Ca was determined at only one other depth at this site, and it proved to be enriched by 70 percent. This behavior contrasts with that at Site 147 where the deepest sample was the most depleted, but is similar to patterns seen at a few sites from previous legs, for example, Sites 26 and 30, Leg 4 (Presley and Kaplan, 1970). Site 148 also shows this pattern, with Ca concentration gradually decreasing down to a depth of 78 meters where the value is only 42 percent that of seawater, then increasing so that the deepest sample has returned to a concentration near that of seawater.

Thus, two mechanisms work to change the Ca ion concentration. One, sulfate reduction, decreases it, presumably by precipitating CaCO<sub>3</sub>. The other is some incompletely understood "ion exchange" phenomenon which increases the Ca ion concentration while decreasing that of Mg and K. Clay mineral diagenesis would be expected to have the observed effect (see, for example, Whitehouse and McCarter, 1958). Dolomite formation by replacement of calcite could also contribute to Mg depletion and Ca enrichment.

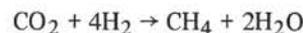
#### Total CO<sub>2</sub> and Delta C<sup>13</sup>

As was noted above, the total carbonate content of the pore water can greatly influence the Ca ion concentration. At Site 147, we found a five-fold enrichment in total CO<sub>2</sub> in the uppermost sample, and an irregular increase to the bottom of the hole at 148 meters depth. At Site 148, our measurements show the total CO<sub>2</sub> concentration increasing from a seawater value near the surface to a three-fold enrichment at a depth of 70 meters. This is approximately the depth of the Ca ion minimum at this site. Below this depth, Ca ion increases and total CO<sub>2</sub> decreases. A somewhat similar situation was found at Site 154, and, in fact, the phenomenon of total CO<sub>2</sub> decreasing while Ca increases has been a common pattern throughout the Deep Sea Drilling Project.

Site 149 presents a complex picture, with Ca showing a smooth increase to values three times seawater at 374 meters depth, but CO<sub>2</sub> giving an irregular pattern. This seems to be related to the complex lithology at this site; the

low CO<sub>2</sub> values found at intermediate depths coincide with a slightly calcareous clay unit lying between units of calcareous nannofossil marl.

Determination of δC<sup>13</sup> in the total CO<sub>2</sub> shows a strong biological influence on nearly all the samples from Leg 15. Most of the samples are isotopically light, due to oxidation of organic matter in the sediment column. This is a phenomenon we have commented on previously (Presley and Kaplan, 1968) and have noted at several sites on other DSDP legs. The opposite pattern, common at previous DSDP sites, has been a tendency for the CO<sub>2</sub> to become isotopically heavier in carbon at depth in the sediment column. This may be caused by a slow equilibration with solid phase carbonates. The CO<sub>2</sub> at depth at Site 147 becomes much too heavy isotopically to explain in this way, however, and is better explained as a hydrogenation of CO<sub>2</sub> to CH<sub>4</sub> in the following way:



Nissenbaum et al. (1972) used this mechanism to explain extremely heavy CO<sub>2</sub> in anoxic sediments from Saanich Inlet, and we have proposed it in our Leg 14 report (Presley et al., 1972) in connection with Site 139 sediments.

#### Silicon

The silicon concentration is similar to what we have found on previous legs, that is, generally higher than in seawater and showing a definite dependence on lithology. This is best shown at Site 149 where a sharp increase at 202 meters depth coincides with the appearance of siliceous fossils and volcanic glass. The concentrations at shallower depths at this site are surprisingly low, for while the sediment is mainly calcareous ooze it is reported to contain a small volcanic component, mostly plagioclase.

#### Lithium

Lithium concentrations have commonly increased with depth in the sediment column at sites on previous legs, and this pattern is maintained at most Leg 15 sites. The largest increase was found at Site 147, where the bottom sample was enriched by five-fold over the normal seawater value. It is unusual to see such a marked enrichment in rapidly depositing basin sediments, because previously high enrichments have been largely confined to areas of thin sediment cover, suggesting an influence by igneous material at depth.

**Boron**

Boron concentrations fall within a fairly narrow range on either side of the seawater value, except for the samples from near the bottom of Holes 147 and 148 which are depleted by about 50 percent. This probably results from boron uptake by clays, but we have no explanation as to why the process is more efficient in some places than in others.

**Manganese**

Manganese is unpredictably variable in concentration, as it has been on all previous legs. We did expect the low values we obtained in the highly reducing sediments at Site 147 because reducing conditions are commonly accompanied by high concentrations of total CO<sub>2</sub> in the pore water, and, presumably, this removes Mn as the carbonate.

Site 149 shows uniformly high dissolved Mn down to a depth of 200 meters and then a drop to uniformly lower values to the bottom of the hole. This corresponds to a change from carbonate ooze to mostly siliceous ooze, but it is not clear why this should effect the Mn concentration.

**Ammonia**

Ammonia concentrations are very high at depth at Site 147, and measurable amount of NH<sub>3</sub> was found in all

samples from Leg 15. This was to be expected, based on our previous experience with DSDP and other samples; Nissenbaum et al. (1972) found up to 14 millimolar NH<sub>3</sub> in reducing sediments from Saanich Inlet, an amount double the highest value we found at Site 147.

If marine organic matter is completely destroyed in the sediment column, the resulting CO<sub>2</sub> should be about six times greater than the NH<sub>3</sub>. No such simple relationship was found in the Leg 15 samples, and probably should not be expected in view of the multitude of complicating reactions possible in the sediment column. CO<sub>2</sub> can be lost as CaCO<sub>3</sub>, as CH<sub>4</sub>, and in other ways, while nitrogen from the organic matter may escape as nitrogen gas, rather than being retained as ammonia.

The Leg 15 samples in general, and the Site 147 samples in particular, clearly show how biological activity can strongly affect the pore water chemistry, both with respect to organic and inorganic constituents.

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